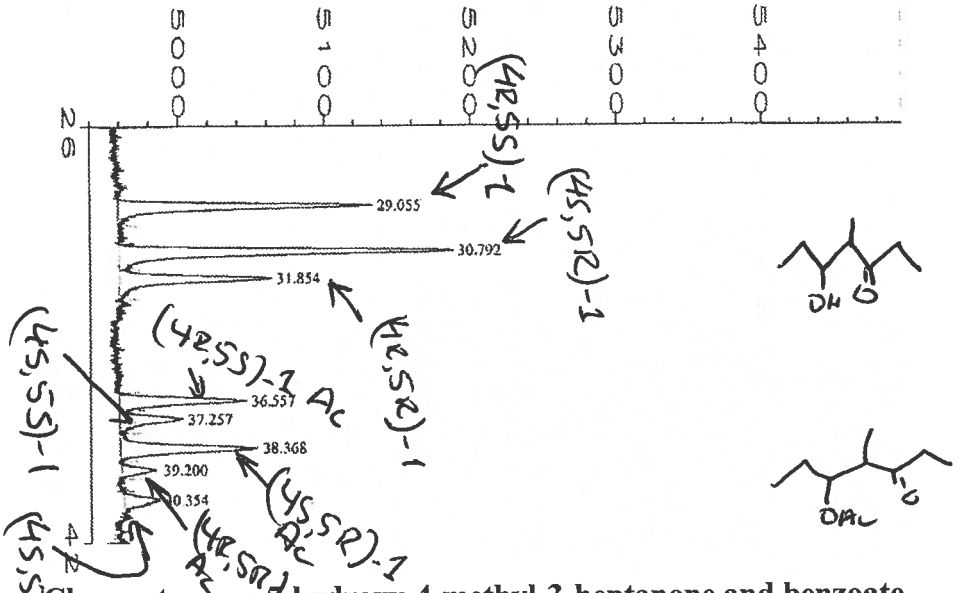
Supplementary information:

Retention times Enantioselective GC CyclosilB

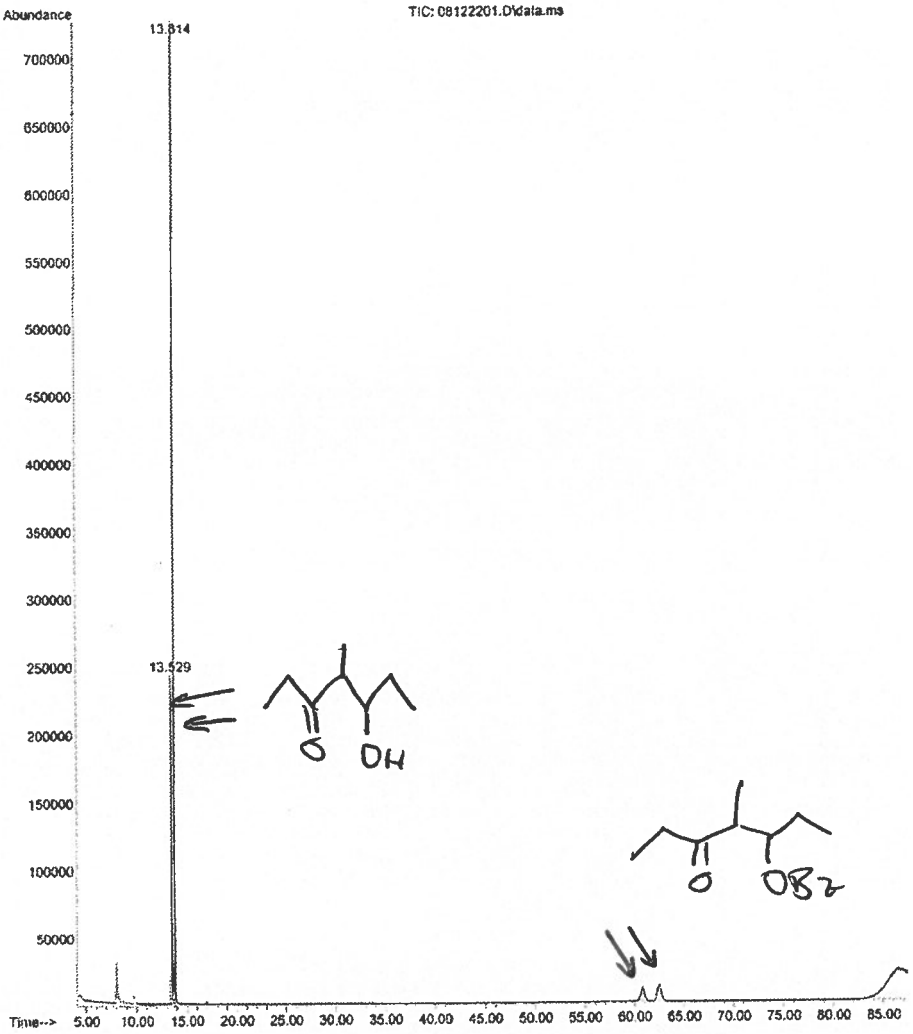
Compound	Temperature (°C)	Retention time (min)
(4*R*,5*S*)-**1**	90	28.0
(4*S*,5*R*)-**1**	90	29.7
(4*R*,5*R*)-**1**	90	30.7
(4*S*,5*S*)-**1**	90	35.7
(4*R*,5*S*)-**1** Acetate	90	35.2
(4*S*,5*R*)-**1** Acetate	90	36.8
(4*R*,5*R*)-**1** Acetate	90	37.8
(4*S*,5*S*)-**1** Acetate	90	39.1
(*S*)-**2**	92	19.5
(*R*)-**2**	92	20.4
(*S*)-**2** Acetate	92	31.2
(*R*)-**2** Acetate	92	32.9
(5*S*,6*S*)-**4**	80	58.6
(5*R*,6*R*)-**4**	80	60.3
(5*R*,6*S*)-**4**	80	64.5
(5*S*,6*R*)-**4**	80	65.3
(5*S*,6*S*)-**4** Acetate	80	71.7
(5*R*,6*R*)-**4** Acetate	80	76.1
(5*R*,6*S*)-**4** Acetate	80	69.3
(5*S*,6*R*)-**4** Acetate	80	73.3

Due to the late elution of benzoates, they eluted in the area where bleeding of the enantioselective column was observed. Therefore the diastereomeric composition of the benzoate esters were determined by GC-MS on the achiral BPX-70 column.

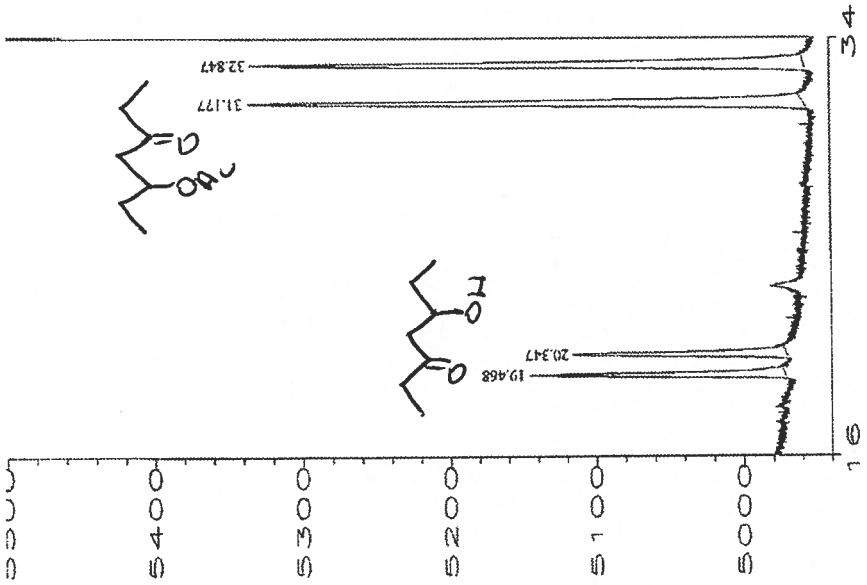
Chromatogram 5-hydroxy-4-methyl-3-heptanone and the acetate ester
CyclosilB, 89°C



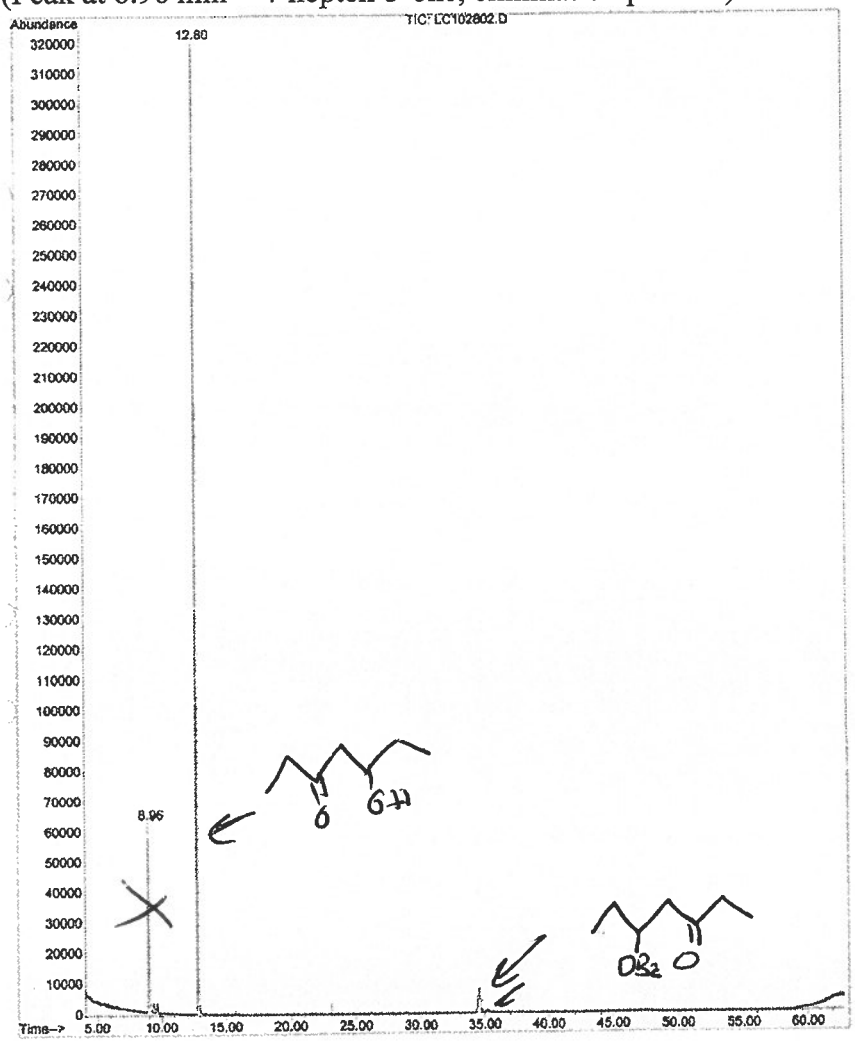
Chromatogram 5-hydroxy-4-methyl-3-heptanone and benzoate
GC-MS, BPX-70, 40(4),10/130(65),15/240(1).



Chromatogram 5-hydroxy-3-heptanone and acetate ester
CyclosilB, 92°C

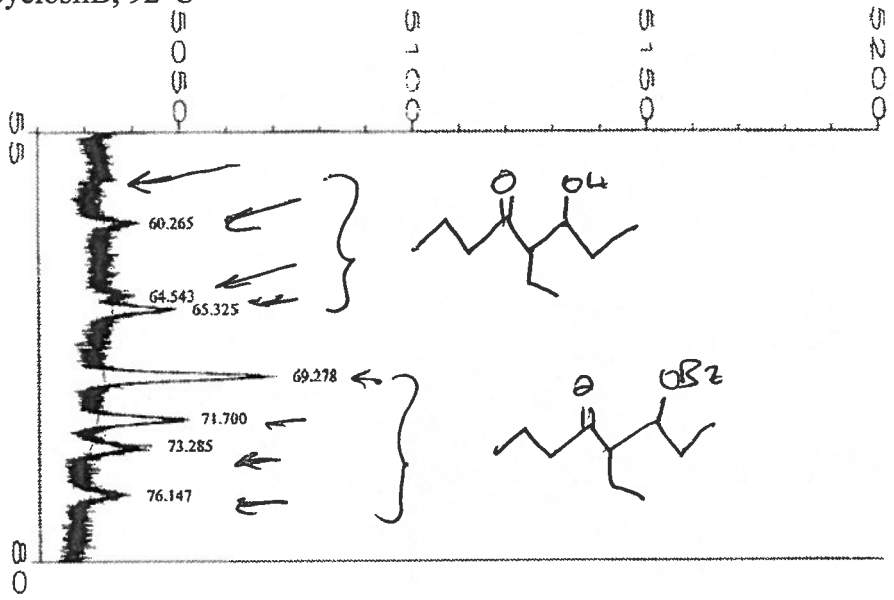


Chromatogram of 5-hydroxy-3-heptanone and benzoate ester
GC-MS, BPX-70, 40(4),10/155(40),15/250(1)
(Peak at 8.96 min = 4-hepten-3-one, elimination product)



Chromatogram 5-ethyl-6-hydroxy-4-octanone and acetate ester

CyclosilB, 92°C



Chromatogram of 5-ethyl-6-hydroxy-4-octanone and benzoate ester

GC-MS, BPX-70, 40(4),10/160(15),15/250(1)